

Use of bentonite and humic acid as modifying agents in alginate-based controlled-release formulations of imidacloprid

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Abstract: In order to prepare a formulation to be used for controlled release, imidacloprid was incorporated into alginate granules by using calcium chloride as gellant. The formulation prepared (alginate–imidacloprid–water) was modified by the addition of different sorbents. The effects on release rate of the addition of natural bentonite desiccated at 105 °C, untreated, acid-treated with sulfuric acid solutions over a concentration range between 0.5 mol dm⁻³ and 2.5 mol dm⁻³, and a commercial humic acid, were studied by immersion of the granules in water under static conditions. The time taken for 50% of the active ingredient to be released into water, (T_{50}), was calculated from the data obtained.

On the other hand, the sorption–desorption processes of imidacloprid from a 0.01 M aqueous calcium chloride solution at 25 °C, by natural, acid-treated bentonite samples, and humic acid, have been studied by using batch experiments in order to evaluate the potential of these materials for their application in controlled-release formulations of pesticides. The experimental data have been fitted to the Freundlich equation in order to calculate the adsorption capacities (K_F). K_F values ranged from 1.76 mg kg⁻¹ for the untreated bentonite up to 126.9 mg kg⁻¹ for the humic acid.

A correlation study was performed with T_{50} , the surface area (S) and the Freundlich parameter (K_F) of the bentonite samples in order to know the factors that affect release rate of imidacloprid from bentonite granules. A linear correlation of the T_{50} values and both S and K_F parameters was observed.

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Keywords: imidacloprid; controlled release; bentonite; humic acid; sorption–desorption

1 INTRODUCTION

The pollution of the water environment with pesticides is effected through their use in the control of aquatic weeds and insects, leaching and run-off from agricultural and forest land, aerial deposition and discharge of industrial waste water.¹ Improper application and/or inappropriate disposal exacerbate the problem. Controlled-release formulations (CRF) have an important potential in reducing the use and impact of pesticides in the environment. The region of Almería in Andalucía (South-eastern Spain) has intensive horticulture based on a raised layered bed system under plastic greenhouses irrigated from underground aquifers. There is concern that aquifers supplying irrigation water are becoming depleted and that these are becoming contaminated with pesticides.² Some evidence exists that some pesticides occur in the Almería well waters.³ CRF can ameliorate pesticide losses including those by leaching, evapora-

tion and degradation.⁴ This has led to considerable effort being put into the development of formulations for the controlled release of chemicals in agriculture.^{5–9} The role of such technology in reducing environmental impact, combined with improving the efficacy of existing and novel pest-control agents will be of great importance in the future.¹⁰ The use of natural materials for this purpose is of special interest in terms of economy and degradability.

Since clays and organic matter are the main constituents of soil that are responsible for its surface properties, investigations with pure clay minerals and organic substances as sorbents have been undertaken to improve our knowledge of the behaviour of pesticides in soils.

Imidacloprid is a new systemic soil and foliar insecticide with a novel mode of action that is widely applied in the Almería region.^{11,12} It is effective for controlling aphids, whiteflies, thrips, scales, psyllids,

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Contract/grant sponsor: CYCYT; contract/grant number: AMB93-0600

Contract/grant sponsor: Accion Integrada; contract/grant number: HB-093 168-B

(Received 20 May 1998; revised version 29 September 1998; accepted 14 December 1998)

Sample	pH	Surface area (m ² g ⁻¹)	Cationic exchange capacity (meq 100g ⁻¹)	Exchange acidity (meq 100g ⁻¹)	Organic carbon (%)
B	8.31	72.7	65.6	22.3	–
B-0.5	2.78	183.0	76.9	67.4	–
B-1.0	2.68	298.8	73.7	71.7	–
B-2.5	3.31	484.8	54.4	50.4	–
H	2.75	13.8	110.0	90.2	35.0

Table 1. Characteristics of sorbents

plant bug, leafhoppers, planthoppers, and other various harmful pest species including resistant strains.

The objective of this study was the evaluation of natural bentonite desiccated at 105 °C, bentonite treated with sulfuric acid solutions over a concentration range between 0.5 mol dm⁻³ and 2.5 mol dm⁻³, and a commercial humic acid, as sorbents in controlled-release formulations of soil-applied pesticides, with the aim of achieving almost any desired rate of release of active ingredient. The factors influencing the controlled release of imidacloprid were examined by studying the interactions between the active ingredient and the sorbents, in particular, the sorption–desorption process of imidacloprid with these sorbents. In addition, correlations between the characteristic release parameter (T_{50}) and bentonite properties such surface area (S) and sorption parameter (K_f) were studied.

2 EXPERIMENTAL METHODS

2.1 Sorbents

The materials used as sorbents for this series of experiments were a natural bentonite (98% montmorillonite, containing sodium as exchange ion) from Almería (Spain) (crushed to a particle size less than 0.15 mm) studied previously by the present authors,¹³ three acid-activated bentonite samples and a commercial humic acid.

Acid activation of the bentonite was carried out in boiling solutions of sulfuric acid (concentrations: 0.5, 1.0 and 2.5 mol dm⁻³) for 1 h. In all cases the resulting samples were heat-treated at 105 °C to constant weight. Chemical composition and textural properties of the samples were also previously studied by the present authors.¹⁴

The three products so obtained, the natural bentonite and the humic acid are referred to as B-0.5, B-1.0, B-2.5, B and H respectively.

Air-dried bentonite samples were analysed by standard methods. pH was determined in a 1+5 sample+water suspension using a glass electrode,¹⁵ surface area was determined from nitrogen adsorption isotherms using a surface analyser from Micromeritics, model II-2370; cation exchange capacity and exchange acidity were calculated using the barium acetate method.¹⁶

The commercial humic acid used was obtained from Fluka Chemie AG (Switzerland). Organic carbon content was determined by the Walkley–Black method,¹⁷ cation exchange capacity, exchange acidity, surface area and pH were determined as above.

All these properties of the bentonite samples and humic acid are shown in Table 1.

2.2 Preparation and evaluation of controlled-release formulations

Imidacloprid technical grade (99.0%) was provided by Bayer Hispania Industrial, Spain; its molecular formula and selected properties are as follows:¹⁸ Molecular formula: C₉H₁₀ClN₅O₂; relative molecular mass: 255.7; melting point: 143.8 °C; vapour pressure (20 °C): 4×10^{-7} mPa; water solubility (20 °C): 0.61 g dm⁻³.

Sodium alginate (medium viscosity: 3500 cps for 2% solution) was obtained from Sigma Chemical Co (St Louis, MO, USA).

The formulations prepared were based on the gelling properties of the alginate in the presence of divalent cations. Formulations containing different percentages of sodium alginate (A), natural bentonite (B), acid-treated bentonite samples (B-0.5, B-1.0, B-2.5), humic acid (H) and technical imidacloprid (I) were made up in water. The rate used and pH values are shown in Table 2. The mixture was vigorously stirred for one hour, the pH range of these moderately viscous formulations being 4.06–7.71.

The mixture (0.05 dm³) was then added dropwise to

Table 2. Composition and pH of controlled-release formulations containing imidacloprid

	Imidacloprid (%)	Na-alginate (%)	B (%)	B-0.5 (%)	B-1.0 (%)	B-2.5 (%)	H (%)	Water (%)	pH (±SD)
IAB	1.21	1.87	3.28	–	–	–	–	93.64	7.66±(0.04)
IAB-0.5	1.21	1.87	–	3.28	–	–	–	93.64	4.15±(0.03)
IAB-1.0	1.21	1.87	–	–	3.28	–	–	93.64	4.06±(0.05)
IAB-2.5	1.21	1.87	–	–	–	3.28	–	93.64	4.27±(0.17)
IAB-H	1.21	1.87	3.28	–	–	–	0.05	93.59	7.71±(0.09)
IA	0.54	1.87	–	–	–	–	–	97.59	7.63±(0.13)

a gellant bath of aqueous calcium chloride (0.25M; 0.3 dm³) using the apparatus described by Connick.¹⁹ The resulting beads were allowed to gel in the calcium chloride solution for 5 min and then filtered and allowed to dry, first at room temperature and then in an oven (40°C) to constant weight.

The products so obtained are referred to in the text as IA, IAB, IAB-0.5, IAB-1.0, IAB-2.5 and IAB-H.

The actual concentration of active ingredients in the dry products was determined by dissolving the granules in a tripolyphosphate solution (0.03M) followed by extraction into water + methanol (80 + 20 by volume). The resulting extract was filtered and the pesticide concentration determined by High Performance Liquid Chromatography (HPLC) using a diode-array detector and data station. Using acetonitrile + water (35 + 65 by volume) as eluent and an LC-18 bonded-phase column, imidacloprid was analysed at 270 nm, its wavelength of maximum absorption. External standard calibration was used and three replicates were carried out for each formulation.

2.3 Static tests to determine release profiles

An accurately weighed quantity of granules containing about 9.00 mg of imidacloprid was added for each sample (three replicates) to 0.5 dm³ of distilled water and placed into stoppered conical flasks. Flasks were shaken in a thermostated bath at 25 (±0.1)°C. At different time intervals, aliquots of 0.001 dm³ were removed for determination of imidacloprid by HPLC using the method described above; unused sample portions were returned to the flasks.

In the final stage of the study, granules were removed from each flask to determine the amount of imidacloprid that remained incorporated in the granules. In order to normalise the release profile curves, the total amount of imidacloprid released plus the extracted imidacloprid remaining in the granules was considered to be 100% of active ingredient initially present in the granules.

2.4 Sorption-desorption studies

The sorption experiments were carried out as follows: aqueous calcium chloride solutions (0.01M) containing initial imidacloprid concentrations (C_0) of 2.0, 4.9, 8.7, 11.4, 17.8, 23.7 and 30.7 mg dm⁻³ were

prepared. Amounts of 3.0 g of each bentonite sample, or 0.1 g humic acid sample and 0.025 dm³ of an imidacloprid solution were placed in stoppered conical flasks and shaken in a thermostated shaker bath at 25 (±0.1)°C. Preliminary experiments were conducted for various time intervals to determine when sorption equilibrium was reached. The time required for equilibrium to be reached between imidacloprid sorbed and imidacloprid in solution was 24 h. After shaking, the solutions were centrifuged and the concentration of imidacloprid in the supernatant was determined by HPLC using the method described above. The imidacloprid sorbed was calculated from the difference between the initial and the final solution concentrations. Blanks containing no imidacloprid and three replicates of each sorption point were used for each series of experiments.

Desorption experiments were carried out by adding aqueous calcium chloride solution (0.01M; 0.025 dm³) to the stoppered conical flasks containing the highest initial pesticide concentration ($C_0 = 30.7$ mg dm⁻³), after removal of the sorption supernatant. This system was again shaken for a 24-h period to establish the new equilibrium. This treatment was also followed by centrifugation and determination of the new equilibrium concentration in the supernatant. The amount of imidacloprid desorbed in the first rinse was calculated. This process was repeated three times.

Blanks containing no imidacloprid were used for each case and all desorption experiments were carried out in triplicate. The difference between the analysis of the three replicates was always less than 10%.

3 RESULTS AND DISCUSSION

3.1 Release studies

Characteristics of controlled-release granules containing imidacloprid are presented in Table 3. The granules were generally spherical in shape and the technical grade imidacloprid was readily incorporated in the alginate matrix. The granules were 1.31–2.77 mg in average weight and the percentage average loading for all imidacloprid granules was 11.59.

The addition of bentonite to the alginate formulations led to larger and heavier granules that were more spherical and dried with less aggregation. It is also interesting to note from the data in Table 3 that

	Imidacloprid (%) (±SD)	Ca ²⁺ (%) (±SD)	Yield ^a (%)	Average weight (mg per granule) (±SD)	Encap. effic. ^b (%)
IAB	10.89 (±0.36)	27.5 (±2.04)	9.17	2.42 (±0.06)	82.54
IAB-0.5	12.31 (±0.22)	20.2 (±0.43)	7.79	2.67 (±0.15)	79.30
IAB-1.0	10.68 (±0.28)	23.1 (±0.65)	8.27	2.56 (±0.01)	72.97
IAB-2.5	12.73 (±0.12)	17.6 (±0.65)	8.40	2.77 (±0.06)	88.39
IAB-H	11.69 (±0.03)	32.8 (±1.23)	7.62	2.33 (±0.14)	73.64
IA	11.24 (±0.26)	6.00 (±0.35)	3.60	1.31 (±0.04)	74.67

^a Yield = Weight of dry product × 100/weight of formulation processed.

^b Encapsulation efficiency = amount of pesticide in dry product × 100/amount of pesticide in formulation processed.

Table 3. Indicative parameters of controlled-release products (dry granule) containing imidacloprid

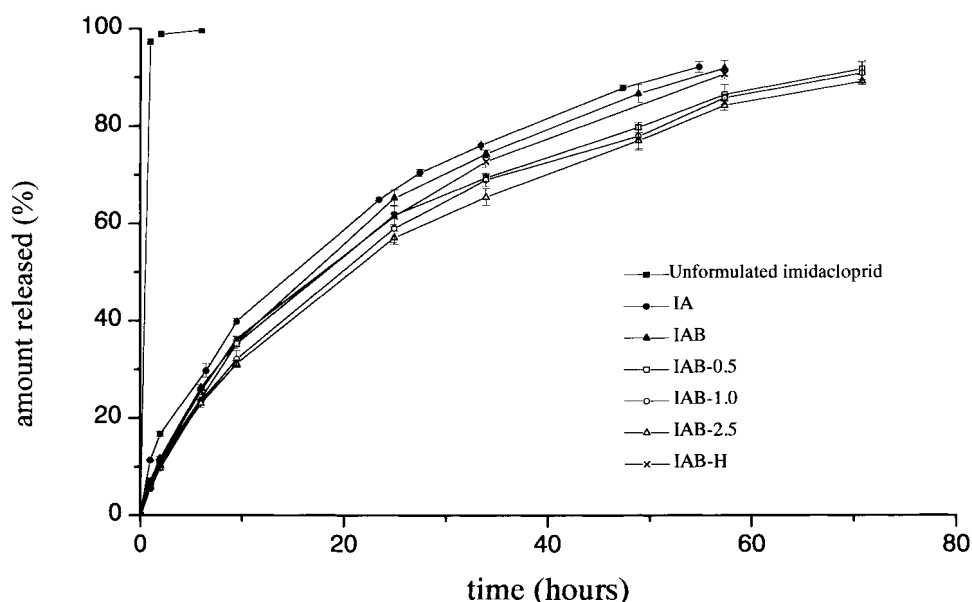


Figure 1. Cumulative release of imidacloprid from granules into static water (error bars represent the standard deviation of three replicates).

inexpensive bentonite effectively increased granule yields and reduced the amount of alginate in the final product, so producing a cheaper formulation.

Figure 1 shows the release profiles for the imidacloprid-alginate granules and the solubility profile for unformulated imidacloprid. As can be seen from the Figure, unformulated imidacloprid dissolved completely within 2 h under the experimental conditions.

The release of imidacloprid from granules fits the empirical equation proposed by Ritger and Peppas²⁰

$$M_t/M_0 = Kt^n \quad (1)$$

where M_t/M_0 represents the fractional release, K is a constant that incorporates characteristics of the macromolecular network system and the drug, and n is a diffusional parameter which is indicative of the transport mechanism.

The values of K and n obtained from initial 60% imidacloprid release are presented in Table 4. There was good correlation of the release profiles of imidacloprid granules with the empirical equation, the correlation coefficient (r) being greater than 0.99.

The values of n ranged from 0.56 for IA granules up to 0.75 for IAB-1.0 granules. A diffusion parameter equal to 0.5 corresponds to Fickian diffusion ($y = kt^{1/2}$) from one-dimensional matrices, but in the case of spheres this has to be corrected for the geometry of the device, the diffusional parameter having a value of 0.43 when Fickian diffusion occurs in a spherical monolithic matrix.²⁰ Values of n close to 0.43 are indicative of Fickian diffusion. The complexity of the heterogeneous system involved, together with the capacity of bentonite samples and humic acid for interacting with the diffusion agent, can explain some of the deviation of n from this value.

The time corresponding to 50% of imidacloprid release, T_{50} , was calculated for the granules using the

Table 4. Constants from fitting the empirical equation $M_t/M_0 = Kt^n$ to release data of imidacloprid into static water

Product	K^a (hours) ⁻ⁿ 10 ²	n^a	r^b	T_{50} (hours)
IAB	7.0 (±0.52)	0.71 (±0.019)	0.999	15.95
IAB-0.5	6.4 (±0.51)	0.72 (±0.021)	0.998	17.38
IAB-1.0	5.7 (±0.48)	0.75 (±0.017)	0.999	18.09
IAB-2.5	5.9 (±0.40)	0.73 (±0.020)	0.999	18.70
IAB-H	7.1 (±0.50)	0.69 (±0.023)	0.999	16.93
IA	11.2 (±0.40)	0.56 (±0.009)	0.999	14.46

^a 95% confidence limits in parentheses.

^b Significant at $P=0.001$.

constants from Table 4. The values ranged from 14.5 h for IA granules up to 18.7 h for IAB-2.5 granules, the variation order being:

$$IA < IAB < IAB-H < IAB-0.5 < IAB-1.0 < IAB-2.5$$

The addition of bentonite to alginate-based formulations reduces the rate of release. The effect of acid treatment of the bentonite is also evident, B-2.5 being the sample with most impact on the release. It was therefore interesting after studying the sorption-desorption process of imidacloprid on bentonite and humic acid to investigate a possible correlation of release (using T_{50} values) with the sorption capacity and characteristics of the samples.

3.2 Sorption-desorption studies

The sorption isotherms of imidacloprid on the four samples of bentonite and humic acid studied are shown in Fig 2. According to the initial portion of the curves, these isotherms may be classified, in general, as L type of the Giles classification²¹ which suggests both that the samples have an average affinity for the insecticide imidacloprid and that there is no strong

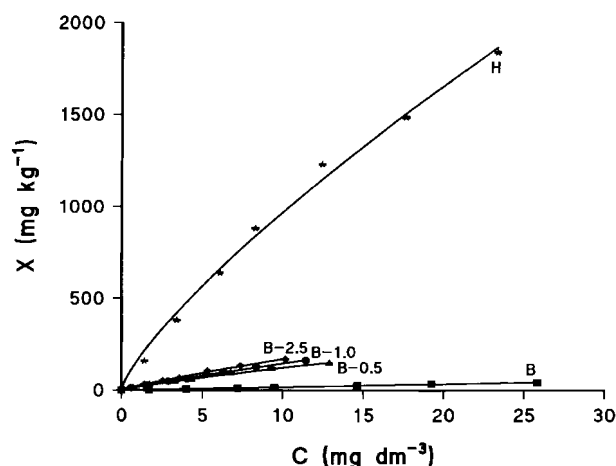


Figure 2. Sorption isotherms for imidacloprid on bentonite samples and humic acid.

competition from the solvent for sorption sites. Nevertheless it can be seen that the slope of the initial portion of the curves increases from the natural bentonite (B) to the acid-treated bentonite samples (B-0.5, B-1.0 and B-2.5), to the humic acid sample. This fact indicates an increasing affinity of the active sites in the sample surface for the imidacloprid molecules,²¹ which might be caused by the acid treatment given to the bentonite samples and by the high organic matter content for the humic acid.

The sorption isotherms in Fig 2 were compared using the K_f parameter of the Freundlich equation.²² The linear form of this equation is

$$\log X = \log K_f + n_f \log C \quad (2)$$

where X is the amount of imidacloprid sorbed (mg kg^{-1} sorbent), C the equilibrium solution concentration (mg dm^{-3}) and K_f and n_f are constants that characterise the sorption capacity for the pesticide. The constant K_f is the amount of pesticide sorbed for an equilibrium concentration of 1 mg dm^{-3} and n is a measure of the intensity of adsorption and reflects the degree to which adsorption is a function of the concentration.^{23,24} The K_f and n_f values were calculated from the least-squares method applied to the linear form of the Freundlich equation and their values are summarised in Table 5. The correlation coefficients

Table 5. Freundlich coefficients, K_f and n_f , for the sorption of imidacloprid on bentonite samples and humic acid

Sample	K_f^a (mg kg^{-1})	n_f^a	r^b
B-N	1.76 (± 0.047)	0.99 (± 0.009)	0.997
B-0.5	15.28 (± 0.296)	0.91 (± 0.008)	0.999
B-1.0	18.90 (± 0.163)	0.88 (± 0.004)	0.999
B-2.5	21.16 (± 0.330)	0.91 (± 0.008)	0.999
HA	126.9 (± 2.96)	0.87 (± 0.008)	0.996

^a 95% confidence limits in parentheses.

^b Significant at $P=0.001$.

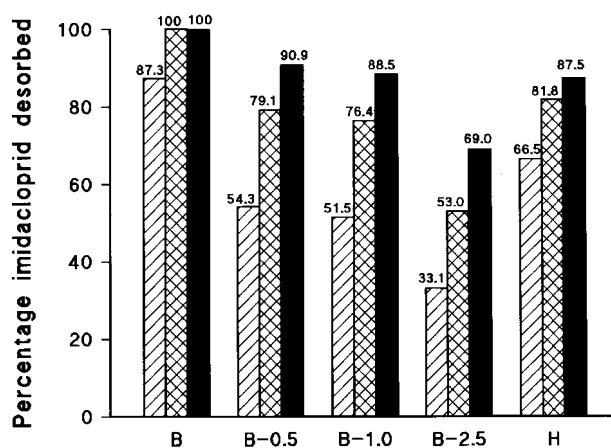


Figure 3. Accumulated percentage of desorbed imidacloprid from the sorbents after three desorption cycles. ▨, Desorption 1; ▩, desorption 2; ■, desorption 3.

coefficients (r) were in all cases greater than 0.99, the correlation being significant at $p=0.001$.

As can be seen from Table 5, the K_f values increased from 1.76 mg kg^{-1} for the natural bentonite to 21.16 mg kg^{-1} for the B-2.5 sample, considering only bentonite samples. The K_f value for the humic acid sample (126.9 mg kg^{-1}) is considerably higher than those corresponding to bentonite samples, due probably to the organic carbon content (35.0%) of this sample. The variation order was:

$$B < B-0.5 < B-1.0 < B-2.5 \ll H$$

The accumulated percentage of desorbed imidacloprid from the different sorbents, after three desorption cycles, is presented in Fig 3. These values range from 69.0% for the sample B-2.5 up to 100% for the sample B. This variation was, in general, inversely related to that obtained for the K_f values. This fact appears to be natural since the sample B-2.5, with a high pesticide sorption capacity, must also present a lesser percentage of desorbed imidacloprid and vice versa.

3.3 Correlation studies

In order to know the factors that affect the release rate of imidacloprid from bentonite-alginate granules, the T_{50} values were correlated with both the surface area (S) and the Freundlich parameter (K_f) of the bentonite samples.

Figure 4 shows the plot of the T_{50} values versus the S and K_f values of the bentonite samples. The analysis indicates that T_{50} values are well-correlated with the K_f values and with the specific surface area of the bentonite samples.

The higher the K_f and S values of the bentonite samples, the higher interactions of imidacloprid with the modifier agents. This fact produces a higher T_{50} value, which means a slower release of the insecticide.

From the linear correlation obtained, the release of imidacloprid from systems of similar structures to those used in our experiments could be readily

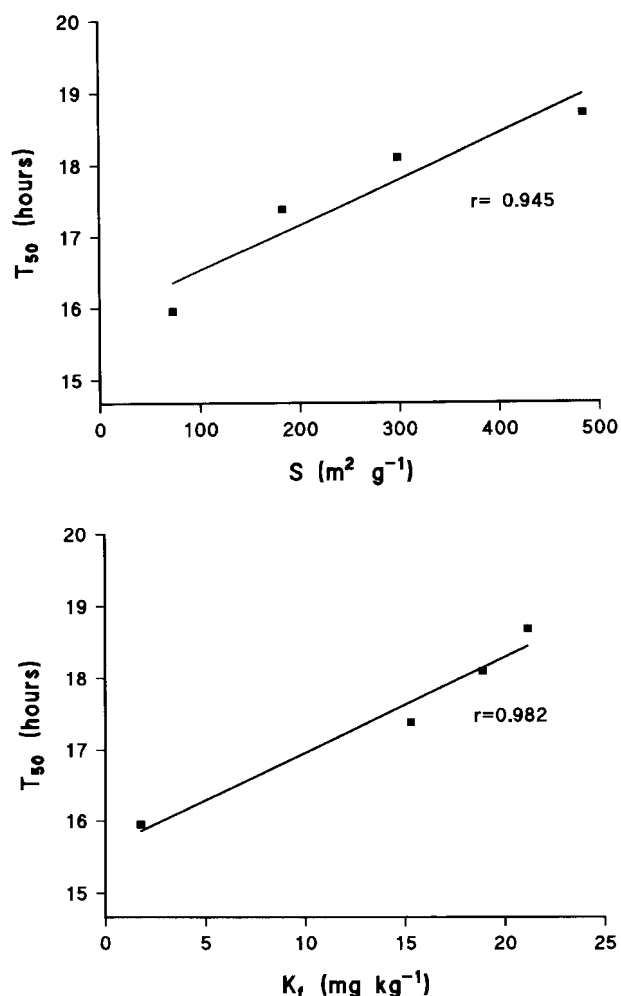


Figure 4. T_{50} values of bentonite granules obtained from static immersion tests versus the Freundlich parameter (K_f) and surface area (S) of the bentonite samples.

predicted from the K_f and S values calculated from the sorption experiments and from characterisation studies of the sorbents.

4 CONCLUSIONS

The experiments indicate that, with the formulations investigated, it is possible to obtain different release rates of imidacloprid by using sorbents properly characterised as modifying agents. The use of bentonite and humic acid as fillers in an alginate-imidacloprid formulation reduces the release of the insecticide compared with a conventional formulation (technical imidacloprid) and with an alginate formulation without sorbents. The addition of bentonite effectively increases the yield of the granules. In addition, in the case of the insecticide-alginate-bentonite formulations, it has been shown that there is a good correlation between the T_{50} value and both surface area (S) and Freundlich parameter (K_f) of the bentonite samples. So, from the S and K_f values of the sorbents used as modifying agents, it could be possible to obtain a rough estimation of the release rate of imidacloprid,

and it may be possible to apply this to any system of similar structure to that used in our studies.

ACKNOWLEDGEMENTS

We thank Bayer Hispania Industrial for samples of imidacloprid. This research was supported by the CICYT Project AMB93-0600 and by Acción Integrada HB-093, 168-B.

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